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Space-selective laser function defects induced by ultra-fast intense laser in LiF crystal

Shoukui Pan*, Benxue Jiang, Hongjun Li, Qingxi Cheng, Xiongwei Jiang, Jianrong Qiu, Congshan Zhu

Photon Craft Project, Shanghai Institute of Optics and Fine Mechanics, Academia Sinica, PO Box 800-211, Shanghai 201800, PR China

Abstract

In an attempt to form space-selective color centers in LiF crystal, photon-induced color centers were continuously created by focusing an ultra-fast intense laser through a microscope objective and translating the LiF crystal sample perpendicular to the axis of the laser beam. The resulting stable color centers region was induced inside the LiF crystal along the path traversed with the focal point of the laser. The measured absorption spectra of color center regions express that it is possible to form space-selective lasing color centers in LiF crystal by the irradiation of ultra-fast intense laser.

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1. Introduction

In contrast, laser damage by visible and IR laser light received little attention owing to the low photon energy at these wavelengths. However, since the mid-1990s people have been strongly interested in the research works on the interaction between the transparent material and near infrared ultra-fast intense laser [1,2].

Ultra-fast intense laser can be used as a powerful tool to clarify some elementary physical chemistry process, such as excitation—energy relaxation and both electron and photon transfer on femtosecond time order and so on. However, when ultra-fast intense laser beam is focused to a spot on the order of optical wavelength, the strength of the power density of such a laser beam can reach $10^{14}\,W/cm^2$ with high time and space resolution. Thus, irradiating the interior of a transparent material with such laser beam, energy was accumulated at a minute region for a short time. Various non-linear optical effects such as

*Corresponding author.
E-mail address: skpan@mail.shcnc.ac.cn (S. Pan).

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two photons and multi-photon ionization, and plasma vibration were induced in the focused region of the laser beam, resulting in a dramatic rise in the temperature and the internal pressure in the region of focus. These effects could not produce a damage like that produced by a long-pulse laser in the material, but they could induce a permanent microscopic modification in material structure at room temperature forming a function microstructure. Up to date, most of the works on this field were concentrated at the interaction between the glass materials (non-crystalline material) and ultra-fast intense laser [3–5]. But according to our working experience in this field, we consider that there are different results when various types of crystalline material interact with the ultra-fast intense laser. Recently, we reported that when a KCl crystal sample was irradiated by femtosecond laser beam, space-selective induced color centers (F centers and aggregate F centers) were formed [6,7]. Thus, we predict that some halide crystals can be interacted with the ultra-fast intense laser to produce crystalline function microstructure. As we know, LiF crystal with F centers and aggregate F centers is a host material of color center laser. Therefore, when ultra-fast intense laser interacts with LiF crystal, it is possible to induce a lasing function microstructure. In this paper, we report some research results on the interaction between the LiF crystal and the ultra-fast intense laser.

2. Experiment

LiF crystal was grown by the Bridgman method. The [0 0 1] oriented LiF crystal samples were cut from the LiF crystal boule. These samples were polished on six surfaces. Fig. 1 is a schematic diagram of an experimental setup for the irradiation by ultra-fast intense laser. The irradiation source we used was a regenerative amplified 800 nm Ti:sapphire laser pumped by the second harmonic of a LD pumped Nd:$LiYF_4$ laser, which emitted laser beam with pulse duration of 120 fs and repetition rate of 1 kHz as well as a maximum energy of 1 mJ per pulse. A LiF crystal sample was put on a sample stage of microscope. The sample

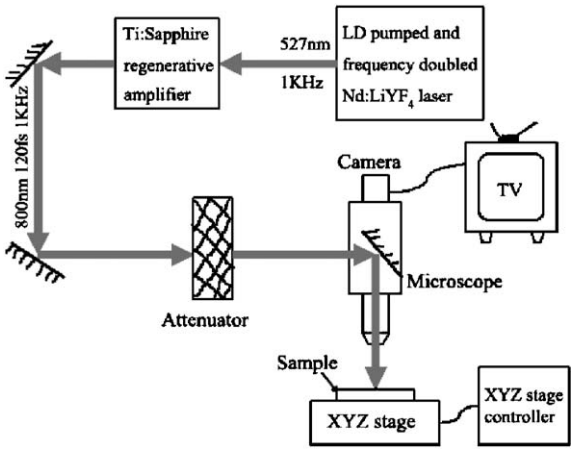

Fig. 1. Schematic of experimental setup for the irradiation by ultra-fast intense laser.

stage was adjustable in three dimensions. The laser beam was focused onto a spot size of about 10 μm and on a plane 1000 or 700 μm below the surface of the sample by the microscope with 5 × objective lens and a numerical aperture of 0.8. Then the sample was translated perpendicular to the axis of the laser beam by moving the sample stage with different rate, which was controlled by a computer. The irradiation power could be adjusted by an attenuator. The resulting color centers region was induced inside the LiF crystal along the path traversed with the focal point of the laser. The selected translating rates of the sample and irradiation power were 50–1000 μm/s and 50–100 mW, respectively. The area of an irradiated region was about 3 mm^2. The absorption spectra of irradiated regions were measured by JASCO V-570 absorption spectrometer.

3. Results and discussions

When the femtosecond laser was operated at irradiation intensity which was lower than the threshold of self-focusing and laser-induce breakdown, multicolor emission occurred at the focused spot, and the brown color of irradiated region was observed. Fig. 2 is a photo of a LiF crystal sample ($11 \times 7 \times 3\ mm^3$) with six regions irradiated with different power and translating rate of the sample.

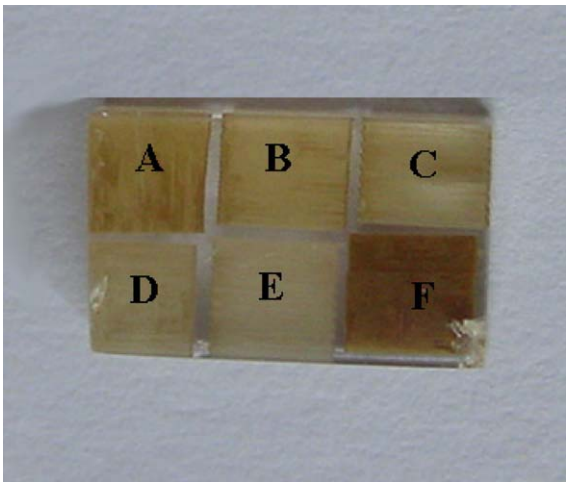

Fig. 2. Photo of a LiF crystal sample with six regions irradiated with different power and translating rate.

They had different brown color (light or heavy) and were denoted as A, B, C, D, E and F, respectively. Table 1 shows the irradiation conditions. We measured the absorption spectra of six different regions and showed them as curves A–F in Fig. 3. There are two obvious absorption peaks near 250 and 446 nm as well as a very weaker one near 343 nm in the absorption spectra of curves A–E. They correspond to F centers, F_3^+ centers and the R_2 transition of F_3 centers in LiF crystal and are related to the brown color of the irradiated regions. Two additional absorption peaks at 429 and 316 nm appear in the absorption spectrum of curve F. They represent the absorption peaks of F_2 centers and the R_1 transition of the F_3 centers in LiF crystal. Fig. 4 is the absorption spectrum of position F in the sample of Fig. 2, which was measured after the sample was laid aside for 1 yr. Making a comparison between the absorption spectrum of curve F in Figs. 3 and 4, the difference of both is very small, so that we consider that F centers and aggregate F centers in LiF crystal are very stable.

F center is formed when the dislocation of a negatively charged ion in crystal lattice leaves an electron trapped in the positively charged vacancy. An F center can thus be visualized as a hydrogen atom embedded in the crystal lattice giving origin to absorption band in the visible range of the spectrum responsible for the coloring of the host crystal. The clustering of these defects leads to the formation of aggregate F centers, which can be visualized as hydrogen molecules with their own distinctive absorption spectra. Usually, they are formed by the irradiation of X-rays or γ-rays or electrons beam, and they can also be produced by the irradiation of violet rays. However, in our results above, the F centers and aggregate F centers were formed by the irradiation of focused near infrared ultra-fast intense laser beam.

After we analyzed the experiment results, we found that the concentration increment of color center was related to the interaction time between the ultra-fast intense laser and LiF crystal: (1) The absorption spectrum of curve E in Fig. 3 represents the result of the fast translating rate of 1000 μm/s and a lower-irradiation power of 50 mW, from which we know that the absorption intensity of its all absorption peaks are the weakest among the absorption spectra of six different irradiated regions, and the absorption spectrum of curve F in Fig. 3 represents the result of the slowest translating rate of 50 μm/s and smallest irradiation power of 48 mW, but the brown color is the heaviest one and absorption intensity is also the highest. We conclude that the slower the translating rate, the heavier the brown color, which means that the concentration of color center increases when the interaction time is increased; (2) Usually, F_3^+ center is easier formed than the formation of F_2 center. However, the absorption band of F_3^+ and F_2 centers in LiF crystal are largely overlapping, the F_2 band peak centered at 429 nm is covered by F_3^+ band (see absorption spectra of curves A–E in Fig. 3). But they are separated in absorption spectrum of curve F, which also expresses that the concentration of F_2 centers increases when the interaction time is increased (because of the slowest translating rate). Thus, these results show us an important technique in this kind of experiment, which is the effect of increasing interaction time (lowering translating rate of sample) and reducing the focused depth is better than increasing the irradiation power.

One considered [4] that the color center generation in glass by the irradiation of femtosecond laser was caused by spectral broadening of the

Table 1
Irradiation conditions for six different irradiated regions

Regions	A	B	C	D	E	F
Irradiation power (mW)	100	100	100	50	50	48
Translating rate (μm/s)	1000	500	200	500	1000	50
Focused depth below the sample's surface (mm)	1.3	1.3	1.3	1.3	1.3	0.7

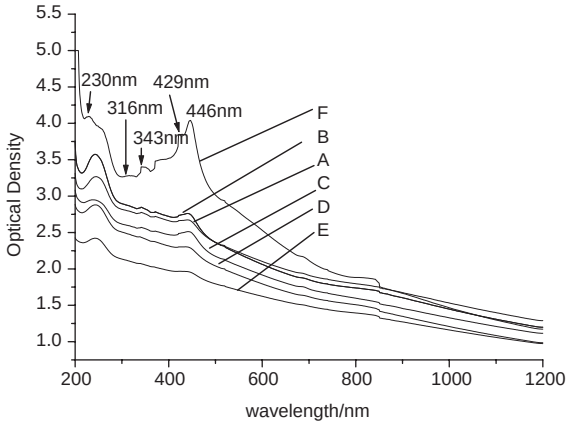

Fig. 3. Absorption spectra of six different irradiated regions in a LiF crystal sample.

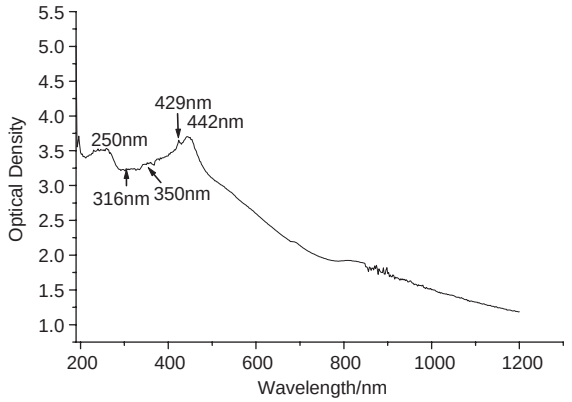

Fig. 4. Absorption spectrum of the region of denoted F in Fig. 2, which was measured after the sample was laid aside for 1 yr.

transmitting laser radiation in the bulk glass, followed by linear or two photons excitation of the glass matrix by the short wavelength portion of the broadened supercontinuum. In our experiments, when the ultra-fast intense laser interacted with LiF crystal, multicolor emission occurred at the focused spot and could be shown on the screen of a TV set. This was a spectral broadening phenomenon of the transmitting laser radiation in LiF crystal. The color center formation in LiF crystal by the irradiation of the ultra-fast intense laser might also be caused by linear or two photons excitation of LiF crystal by the short wavelength part of the broadened supercontinuum. And in the experiments, lowering translation rate, in fact, increased interaction time between the ultra-fast intense laser and LiF crystal so that the total dose of irradiation of the short wavelength part of the broadened supercontinuum was increased, resulting in the concentration increment of color center. The observed effect shown in curve F in Fig. 3 was evident, 10 times higher dose of irradiation induced large effect (the heaviest brown color).

As we know [8], the F_2 and F_3^+ centers are the color centers with laser effect. Usually F_2^+ and F_2^- centers in LiF crystal are also the color centers with laser effect, but their absorption peaks did not appear in the absorption spectrum. We think that the concentration of F_2^+ and F_2^- centers was not enough because the thickness of the irradiated layer was very thin.

4. Conclusion

We realized the space-selective induced color center in LiF crystal by the irradiation of near infrared ultra-fast intense laser. The observed color centers were the F, F_2, F_3 and F_3^+ centers, among which F_2 and F_3^+ centers were the color centers with laser effect. The absorption peaks of F_2^- and F_2^+ centers did not appear in the absorption spectrum because the irradiated layer

was very thin. The concentration increment of color center in LiF crystal was related to the interaction time between the ultra-fast intense laser and LiF crystal. The longer the interaction time, the higher was the concentration.

Acknowledgement

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